Published online August 4, 2005

Reproduced from Soil Science Society of America Journal. Published by Soil Science Society of America. All copyrights reserved.

Mineralogy in Relation to Phosphorus Sorption and Dissolved Phosphorus Losses in Runoff

C. J. Penn,* G. L. Mullins, and L. W. Zelazny

ABSTRACT

The relationship between soil test P (STP) and dissolved reactive P (DRP) in runoff has been shown to vary with soil type due to differences in soil properties. This study was conducted to determine the effect of mineralogy on P sorption behavior and DRP losses in runoff using simulated rainfall. Nine different soil types were sampled from four different fields to provide a range in STP. Unamended soils were packed into runoff boxes for use in a rainfall simulation study (7.5 cm h^{-1} for 30 min). A mineralogical analysis and adsorption-desorption isotherm was conducted on one representative sample from each soil type. Results indicated that P retention for adsorption and desorption in separated clay fractions and whole soils was well correlated to Al bearing minerals such as hydroxy-interlayered-vermiculite (HIV), gibbsite, and amorphous Al. However, P retention was negatively related to kaolinite content, which was also confirmed by isotherms conducted on pure clay minerals. Based on the isotherm results, all soils were split into two groups based on the ratio of HIV/kaolinite. Soils with a HIV/kaolinite ratio >0.5 had a significantly lower concentration of DRP in runoff for a given soil water soluble P level compared with soils with a ratio <0.5.

Phosphorus losses from agricultural soils to surface waters have been of recent public concern due to the negative effects of increased P concentrations on surface water quality (Sharpley et al., 2000). Agricultural soils considered high in P can cause significant movement of P into waterways in the form of dissolved P and particulate P (Sims, 1998). Although erosion control has been shown to decrease total P and particulate P losses (Quinton et al., 2001), significant concentrations of dissolved P can occur in runoff from soils where erosion is kept at a minimum, particularly from soils that are high in STP or having received recent P applications (Sharpley et al., 1978; Daniel et al., 1994; Daverede et al., 2003). Dissolved P concentrations in surface runoff from unamended soils are typically much less relative to P losses from soils that have recently received P amendments (Moore et al., 2000), However, significant dissolved P losses can occur from high P, nonamended soils (Pote et al., 1996; Schroeder et al., 2004).

With the established link between STP concentrations and dissolved P losses in runoff (Sims et al., 2002), many model and risk indicators of P loss have incorporated the relationship between some measure of soil P and runoff dissolved P (Gburek et al., 2000; Coale et al., 2002; Vadas et al., 2002). However, recent research has shown that this relationship will vary based on soil type (Sharpley, 1995; Sharpley et al., 1996; Pote et al., 1999; Torbert et al., 2002). Therefore, an understanding of how different soil properties affect P concentrations in solution, leachate, and runoff is necessary to determine the effect of soil type on the relationship between STP and runoff P losses.

One of the most influential soil properties in regard to P sorption is soil clay content, which has often been correlated to P sorption parameters (Fox and Kamprath, 1970; Loganathan et al., 1987; Solis and Torrent, 1989; Bennoah and Acquaye, 1989). However, it is the high surface area and presence of various P sorbing minerals that results in the common observation that high clay soils often adsorb more P compared with coarse-textured soils (Loganathan et al., 1987). Phosphate sorption is attributed primarily to ligand exchange reactions between hydroxyls exposed on surfaces of minerals and the phosphate molecule in soil solution. The mineralogy of a soil will take into account both surface area (due to the fact that most phyllosilicates and oxides/hydroxides each have a specific range in surface area) and the Fe/Al content of a soil. Therefore, analysis of mineral types and content should provide an estimate of potential P-sorption sites (Jones, 1981; Sposito, 1984; Parfitt, 1989) and the potential for a soil to release P into runoff. Variation in surface area and differences in the ability of different minerals to retain P should be responsible for the observed differences in the relationship between soil P levels and runoff dissolved P concentrations among soil types.

Although there has been significant work conducted on P adsorption in regard to soil mineralogy, few mineralogical studies have been performed in conjunction with P desorption isotherms or runoff studies. The objectives of this study were to (i) investigate the role of soil mineralogy on P adsorption/desorption behavior in Virginia soils, and (ii) relate soil mineralogy and adsorption–desorption behavior to potential dissolved P losses in surface runoff from Virginia soils.

MATERIALS AND METHODS

Nine soil types were chosen to represent the major agricultural soils of the Piedmont, Coastal Plain, and Ridge and Valley physiographic provinces of Virginia. Among each soil type, four different soils (i.e., locations) were collected to provide a range in Mehlich-1 extractable P (M1-P) from below

C.J. Penn, USDA-ARS, PSWMRU, 3702 Curtain Rd., University Park, PA 16802; G.L. Mullins and L.W. Zelazny, Dep. of Crop, Soil, and Environmental Sciences, Virginia Tech, 330 Smyth Hall, Blacksburg, VA 24061. Received 2 July 2004. *Corresponding author (cjp124@psu.edu).

Published in Soil Sci. Soc. Am. J. 69:1532–1540 (2005).
Pedology, Soil Mineralogy, Soil Chemistry, Soil & Water Management & Conservation
doi:10.2136/sssaj2004.0224
© Soil Science Society of America
677 S. Segoe Rd., Madison, WI 53711 USA

Abbreviations: DRP, dissolved reactive P; HIV, hydroxy-interlayered vermiculite; M1-P, Mehlich-1 phosphorus; subscript [ox], ammonium oxalate extractable; STP, soil test phosphorus; WSP, water-soluble phosphorus.

Reproduced from Soil Science Society of America Journal. Published by Soil Science Society of America. All copyrights reserved.

moderate (<18 mg kg^{-1}) to very high (>55 mg kg^{-1}) agronomic P levels (Virginia Dep. of Conservation and Recreation [DCR], 1995). One exception to this was the Bojac soil type (only three different M1-P levels were located for this soil). Bulk samples were collected from cooperating farmer's fields that had not received any organic amendments or P additions within 1 yr before collection.

The Piedmont soils used in this study consisted of Cecil (Fine, kaolinitic, thermic Typic Kanhapludults), Tatum (Fine, mixed, semiactive, thermic Typic Hapludults), and Davidson (Fine, kaolinitic, thermic Rhodic Kandiudults) series. Coastal plain soils used consisted of Emporia (Fine-loamy, siliceous, subactive, thermic Typic Hapludults), Slagle (Fine-loamy, siliceous, subactive, thermic Aquic Hapludults), and Bojac (Coarse-loamy, mixed, semiactive, thermic Typic Hapludults) series. The Ridge and Valley soils chosen for this experiment were Frederick (Fine, mixed, semiactive, mesic Typic Paleudults), Groseclose (Fine, mixed, semiactive, mesic Typic Hapludults), and Sequoia (Fine, mixed, semiactive, mesic Typic Hapludults) series.

Each sample was collected by removing soil from the surface 0- to 5-cm layer and sieving through a 19-mm sieve before being air-dried for use in the rainfall simulation study. Samples were sieved to 2 mm for the following characterization: pH (1:1 soil/water ratio), sand, silt, and clay analysis by the hydrometer method (Day, 1965), and water-soluble P (WSP 1:10 soil/deionized water, 1-h reaction time, filtration with 0.45-μm Millipore membrane [Kuo, 1996]). Soil test P was analyzed by Mehlich-1 (M1-P: 1:4 soil: 0.05 *M* HCl + 0.0125 *M* H_2SO_4, 5-min reaction time, filtration with Whatman #2 paper [Kuo, 1996]). Mehlich 1-P and WSP solutions were analyzed for P by inductively coupled plasma emission spectroscopy (SpectroFlame Modula Tabletop ICP; Spectro Analytical Instruments, Inc., Fitchburg, MA).

Phosphorous Adsorption and Desorption Experiments

For each soil type, one sample was chosen for use in a P adsorption and desorption experiment (Table 1) that was conducted on both whole soils and the separated clay fraction from each soil. Clay fractions were separated from whole soils as described in the *Soil Mineralogical Analysis* section below. Individual samples within each soil type were chosen based on their measured WSP concentrations (average WSP was 7.75 mg kg^{-1}) with the intent of obtaining a set of samples that are relatively uniform to prevent soil WSP from being a confounding factor (Table 1). In addition to the whole soils and clay fractions, the sorption experiments were conducted on several mineral source materials; (i) synthetic goethite (yellow 920Z, Bayer Corp.; Krefelt, Germany), (ii) synthetic hematite (red 1120Z, Bayer Corp.; Krefelt, Germany), (iii) synthetic gibbsite (RH-31F, Reynolds Metals Co., Bauxite, AK), (iv) well crystalline kaolinite from Washington County, GA (Source Clay Minerals Repository, Clay Minerals Society), and (v) poorly crystalline kaolinite from Warren County, GA (Source Clay Minerals Repository, Clay Minerals Society).

A single point P adsorption isotherm was conducted by adding 34 mL of 0.01 *M* $CaCl_2$ and 6 mL of 100 mg P L^{-1} solution (KH_2PO_4) to 50-mL centrifuge tubes containing 0.4 g of sample (1.5 mg P added per 1 g of sample). Samples were duplicated and placed on a reciprocating shaker for 24 h. Solutions were centrifuged at 1800 × *g* (2000 rpm) for 10 min and then filtered through a 0.45-μm Millipore membrane and analyzed for P by the Murphy–Riley method (Murphy and Riley, 1962). Percentage of P adsorbed was then calculated as the difference between P added and P left in solution (% of added P that was adsorbed). Phosphorus saturated samples from the single point adsorption isotherms were then used in the desorption isotherm by sequentially desorbing the samples four consecutive times with 40 mL of 0.01 *M* $CaCl_2$ and shaking for 1 h. After each successive desorption, samples were centrifuged, filtered, and analyzed for P as previously described for the single point P adsorption. The total amount of P desorbed was used to calculate the percentage of P retained after four desorptions as follows:

$$\frac{\text{Adsorbed P after four desorptions}}{\text{P adsorbed from single point isotherm}} \times 100 \quad [1]$$

Table 1. General properties of soils used for the P sorption and mineralogy study.

Soil type	WSP	Mehlich-1 P	pH	Clay	Al_{ox}	Fe_{ox}
	mg kg^{-1}			%	mg kg^{-1}	
Cecil	7.56	57	5.14	29.9	547	453
Tatum	6.89	41	6.57	27.9	555	1511
Davidson	7.68	19	6.29	29.4	840	1659
Emporia	7.71	33	5.35	10.9	331	152
Slagle	8.4	37	6.11	14.9	240	110
Bojac	7.73	45	6.57	16.9	739	772
Frederick	11.85	85	7.07	24.2	628	712
Groseclose	5.62	11	6.25	17.9	809	1162
Sequoia	6.35	23	6.30	40.0	705	1816
$LSD_{0.05}$†	1.49	4	0.51	2.6	59	125

† LSD, least significant difference. Differences between means greater than the LSD indicate significant differences at $p < 0.05$.

Soil Mineralogical Analysis

Mineralogical analysis was conducted on the same nine samples used in the adsorption and desorption experiment. Pretreatments for mineralogical analysis included removal of organic matter with 30% (v/v) H_2O_2 buffered at pH 5 with 1 *M* sodium acetate (Kunze, 1965). Sand was separated by wet sieving through a 50-μm sieve, while silt and clay fractions were separated by centrifugation and decantation using 0.1 *M* Na_2CO_3 (pH 9.5) as a dispersant. X-ray diffraction was used to determine clay mineral suites present by analyzing oriented K saturated samples with no heat treatment and after heating for 4 h at 110, 300, and 550°C. Samples were scanned at a fixed counting time of 4 s at a 0.075° 2θ with a Scintag XDS 2000 X-ray diffractometer (Scintag, Madison, WI) using CuKα radiation (40 mA, 45 kV). Subsamples of the K saturated clay fractions were also analyzed for weight loss by thermogravimetric analysis (TGA) from 25 to 1000°C using a TGA 2950 (TA instruments, NewCastle, DE). Amorphous Al and Fe (Al_{ox} and Fe_{ox}, respectively) for both clay fractions and whole soils were determined by ammonium oxalate extraction (1:40 ratio of soil to 0.2 *M* ammonium oxalate [pH 3], 2-h reaction time in the dark and filtration with Whatman #42 paper [McKeague and Day, 1966]). Resulting extracts were analyzed for Al and Fe by ICP–AES. Total surface area of Ca saturated whole soils was determined using ethylene glycol monoethyl ether (EGME) as described by Carter et al. (1965).

Rainfall Simulation Study

Dried and sieved soils were poured into wooden runoff boxes 100 cm long, 20 cm wide, and 5 cm deep (SERA-17, 2004), replicated three times, leveled, and presaturated 24 h before being placed under a rainfall simulator to ensure that runoff would occur during the rainfall event. The amount of water necessary to presaturate each soil type was determined by adding water to one box for each soil until ponding on the

Reproduced from Soil Science Society of America Journal. Published by Soil Science Society of America. All copyrights reserved.

soil surface occurred. That same volume of water was then applied to all boxes containing the respective soil type.

The rainfall simulator consisted of a single "Tee Jet" HH-SS-50WSQ nozzle (Spraying Systems, Wheaton, IL) attached to a 3 m × 3 m × 3 m metal frame, and calibrated to achieve an intensity of 7.5 cm h^{-1} at 90% uniformity (SERA-17, 2004). The runoff boxes were placed randomly under the rainfall simulator on steel racks adjusted to a 5% slope. Rainfall events were 30-min long and all runoff was collected in 9-L plastic containers (one runoff sample from each box). Subsamples of the bulk runoff were taken for DRP analysis by removing 40 mL from the mixed bulk sample and filtering through 0.45-μM Millipore filter papers followed by P analysis by the Murphy and Riley colorimetric method (Murphy and Riley, 1962).

Statistical Analyses

The distribution of data was tested for normality by the Shapiro–Wilkes statistic conducted by the "Univariate" procedure of the Statistical Analysis System, Version 8.0 (SAS Institute, 1999). All correlation and analysis of variance procedures were conducted by standard procedures of SAS. Multiple linear regression was conducted using the "stepwise" procedure of SAS.

RESULTS AND DISCUSSION

Soil Properties

General properties of soils used in the P adsorption and desorption experiment are listed in Table 1. The soils used in the mineralogical analysis and the adsorption–desorption experiments had a range of WSP from 5.62 to 11.85 mg kg^{-1} with an average of 7.75 mg kg^{-1}. Although WSP was relatively uniform for the soils used in the experiment, M1-P varied (11–85 mg kg^{-1}) (Table 1). With the exception of the Cecil and Emporia soils, the natural pH ranged from 6.11 to 7.07 (Table 1). This relative uniformity in pH is important since pH can have a strong effect on the charge properties of soils as well as the solubility of Al and Fe, which can in turn influence P behavior. The variation in clay content among soils indicates that the Coastal Plain soils (Emporia, Slagle, and Bojac) possessed the lowest clay content, Piedmont soils (Cecil, Tatum, and Davidson) had the highest, while Ridge and Valley soils (Frederick, Groseclose, and Sequoia) had a clay content intermediate to the Coastal Plain and Piedmont soils (Table 1). One exception to this was the Sequoia soil, which had a much higher percentage of clay (40%) than the other soils. This may be due to the fact that this sample was collected on a steep slope and much of the topsoil may have been eroded leaving the subsoil exposed. Support for this conclusion lies in that the Sequoia sample contained much higher amounts of mica (which often occurs in the subsoil) compared with the other soils (Fig. 1a).

X-ray diffraction patterns conducted on the K saturated clay fraction at 25°C (Fig. 1a) indicated that Cecil and Tatum soils contained the highest amounts of kaolinite compared to the other soils. Quartz appeared in every soil except Slagle (Fig. 1a). Because chlorite and HIV share the same peak at 25°C, the samples were heated to 550°C to partially collapse HIV to approximately 1.1 nm. At this temperature, chlorite maintains a 1.4-nm peak and it is then possible to distinguish between the two minerals. Appreciable amounts of HIV occurred in every sample while it was a minor component of Cecil, Tatum, and Sequoia. Tatum was the only soil containing any appreciable amount of chlorite (Fig. 1b). Thus, the 1.4-nm peaks at 25°C for all soils except for Tatum are primarily attributed to HIV (Fig. 1a). The presence of mica was evident only in the Sequoia, Groseclose, and Tatum soils, with what appeared to be a greater quantity in the Sequoia compared with the other two soils based on the height and area under the peak. In addition, the data in Table 1 indicates that all soils contained a greater amount of Fe_{ox} than Al_{ox} except for the Cecil, Emporia, and Slagle. Overall, the mineralogical makeup of these samples in regard to P chemistry was dominated by kaolinite, HIV, amorphous Al and Fe (estimated by ammonium oxalate extraction) and crystalline Fe (estimated by TGA), and is considered typical for Virginia soils. Of these minerals, amorphous Fe and Al are considered the most important in regard to P sorption followed by goethite, kaolinite, and 2:1 clay minerals such as HIV (Jackman et al., 1997; Juo and Fox, 1977).

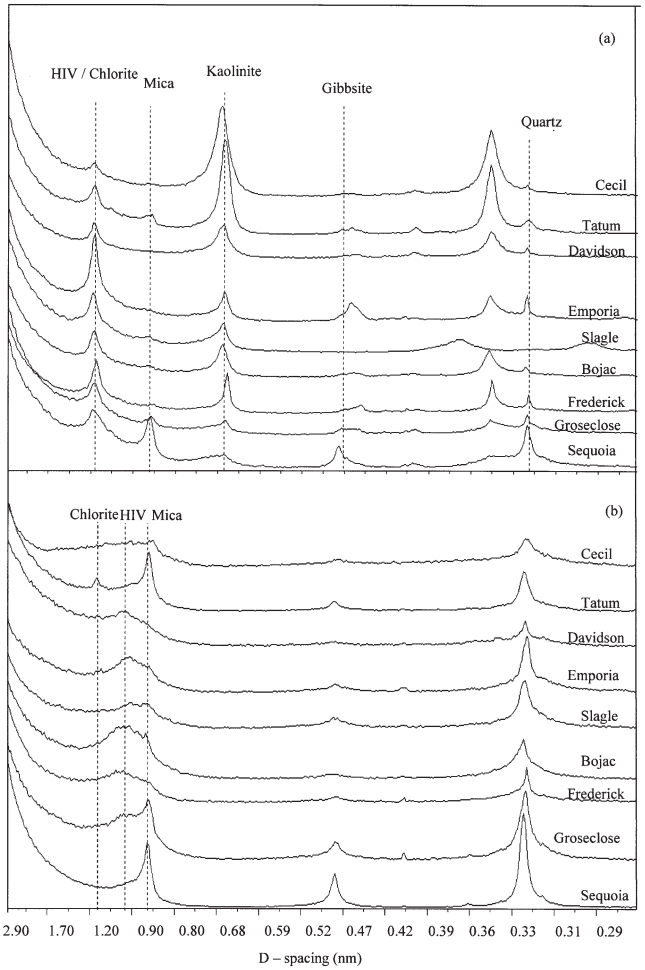

Fig. 1. X-ray patterns for the nine soils used in the P sorption study conducted on (a) room temperature samples and (b) samples heated to 550°C.

Reproduced from Soil Science Society of America Journal. Published by Soil Science Society of America. All copyrights reserved.

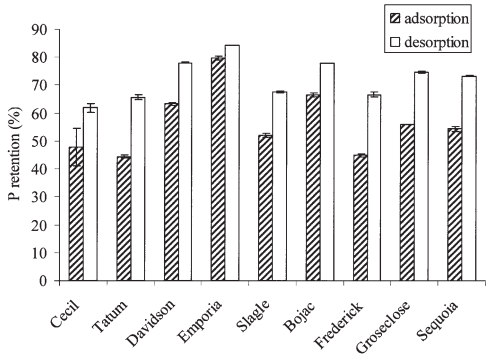

Fig. 2. Phosphorus retention by the separated clay fractions of each soil type expressed as the percentage of added P that was absorbed during a single point isotherm (adsorption). Desorption expressed as P retained on samples after four sequential desorptions with 0.01 *M* $CaCl_2$ ([P remaining on clay fraction after four desorptions/ P remaining on clay fraction after previous single point adsorption] × 100). Error bars indicate standard deviation. Least significant difference at $P < 0.05$ was 5.4 and 1.5 for adsorption and desorption, respectively.

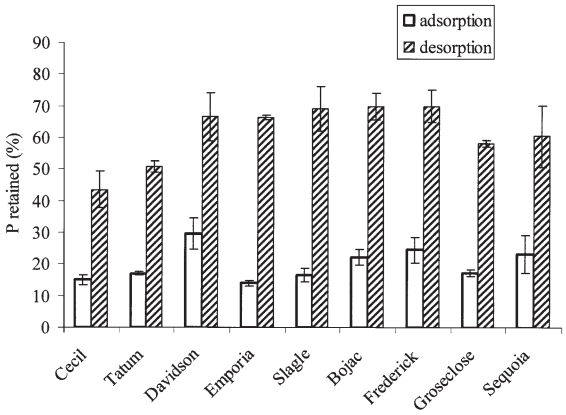

Fig. 3. Phosphorus retention by whole soils expressed as the percentage of added P that was absorbed during a single point isotherm (adsorption). Desorption expressed as P retained on samples after four sequential desorptions with 0.01 *M* $CaCl_2$ ([P remaining on soil after four desorptions/P remaining on soil after previous single point adsorption] × 100). Error bars indicate standard deviation. Least significant difference at $P < 0.05$ was 7.3 and 12.7 for adsorption and desorption, respectively.

Phosphorus Adsorption and Desorption

The greatest amount of P per unit weight of clay was absorbed by the separated clay fraction of the Davidson, Emporia, and Bojac soils as indicated by the single point isotherm (63, 80, and 67% P adsorption, respectively; Fig. 2). Data presented in Fig. 2 also shows that the Cecil, Tatum, and Frederick soils adsorbed the lowest amount of added P (48, 44, and 45% P adsorption, respectively) while the Slagle, Groseclose, and Sequoia soils were intermediate between the two groups (52, 56, and 54% P adsorption, respectively; Fig. 2). Not only were the Davidson, Emporia, and Bojac clay fractions able to adsorb the most P, these samples also retained the highest percentages of the adsorbed P after four sequential desorptions (78, 84, and 78% P retained, respectively; Fig. 2). Clay fractions of soils that adsorbed less P also desorbed more P when compared with the other soils (i.e., Cecil, Tatum, and Frederick). In an attempt to relate mineral type and quantity to P sorption, we correlated the mineral content as quantified by TGA to the amounts of P retained after the single point P addition and four sequential desorptions (Table 2). Pearson correlation coefficients (as determined using SAS) indicated that HIV and amorphous Al as determined by ammonium oxalate extraction were the only significant variables related to P adsorption (Table 2). Retention of P after four sequential desorptions was also significantly related to HIV, amorphous Al, and gibbsite. In addition, kaolinite possessed a significant and negative relationship with P desorption (Table 2). These results suggest that HIV and amorphous Al can adsorb high amounts of P as well as retain the adsorbed P throughout sequential desorptions, while kaolinite is not able to retain P as strongly.

As expected, the results of the single point P adsorption isotherm and sequential desorption isotherm conducted on the whole soils was different from that of the clay fractions (Fig. 3). In this case, we observed that the Emporia soil adsorbed the lowest amount of P (14%) compared with the other soils since this soil contained the least amount of clay and next to the lowest amount of Al_{ox} and Fe_{ox} (Table 1). Adsorption of P was clearly the highest among the Davidson, Bojac, Frederick, and Sequoia soils (30, 22, 25, and 23, respectively), while surprisingly the Cecil and Tatum adsorbed lower amounts of P relative to the other soils (15 and 17%, respectively), as was also observed with the clay-sized fractions (Fig. 2 and 3). Unlike P sorption by the separated clay fractions, soils that adsorbed high amounts of P were not necessarily able to retain the adsorbed P following four sequential desorptions in the whole soil

Table 2. Pearson correlation coefficients between the percentage of P retained from a single point isotherm, four sequential desorptions and soil mineral quantity among both clay fractions and whole soils. *, **, indicates significance at the 0.05 and 0.01 probability level, respectively.

	Clay fraction		Whole soil	
Soil parameter	% P retained from single point P addition	% P retained after four sequential desorptions	% P retained from single point P addition	% P retained after 4 sequential desorptions
gibbsite	0.5	0.67*	0.63*	0.26
Fe oxides	0.22	0.21	0.24	0.28
kaolinite	−0.41	−0.63*	0.21	−0.76*
HIV	0.76*	0.79**	0.92**	0.32
Al_{ox}	0.81*	0.75*	0.67*	0.05
Fe_{ox}	0.44	0.51	0.60	0.18
WSP	na	na	0.28	0.45
% Clay	na	na	0.44	0.45
Surface area g^{-1} clay	na	na	0.66*	0.47

Reproduced from Soil Science Society of America Journal. Published by Soil Science Society of America. All copyrights reserved.

samples (Fig. 3). For example, although the Emporia and Slagle soils adsorbed very little P, these two soils retained nearly 70% of the P adsorbed after four sequential desorptions. Again, P retained after four desorptions from the whole soils indicated that the Cecil and Tatum retained the least amount of adsorbed P per unit weight compared with the other soils.

The Cecil and Tatum were among the highest in clay content, suggesting that clay content for these soils was not a significant variable in explaining P adsorption and desorption. Evidence for this is shown in Table 2 in that clay content of the soils was not significantly correlated with P adsorption or P retained after four sequential desorptions. This result is in contrast to previous studies that showed that clay content was well related to the amount of P required to reach 0.2 mg P L^{-1} in solution (Fox and Kamprath, 1970; Loganathan et al., 1987). For example, Mozaffari and Sims (1994) reported that single point P isotherm values were significantly correlated with clay content (r = 0.90***). In our case, the lack of correlation between clay content and P retention suggests that mineral type and quantity may be more important than the total amount of clay-sized particles present in soil. Evidence for this is shown in Table 2 in that gibbsite, HIV, and amorphous Al were significantly related to P adsorbed, similar to results of the clay-sized fraction (Table 2).

Surface area per gram of clay was also well related to P adsorption. The significant relationship of P adsorption with surface area per gram of clay and not with clay content occurred because different minerals vary in surface area (Van Olphen and Fripiat, 1979). As a result, soils with similar clay contents can possess very different surface areas and thus different P adsorption capacities. The data in Table 2 indicates that the only mineral related to P retention after four sequential desorptions was kaolinite (negative relationship), thus soils with higher levels of kaolinite were not able to retain P as tightly compared with the other soils. Note also that the soil WSP content did not appear to be a confounding factor as indicated by the lack of a significant relationship between P sorption and soil WSP concentration (Table 2).

Differences in Phosphorus Sorption between Mineral Types

Overall observation of the Pearson correlation coefficients for the separated clay fractions and whole soils (Table 2) suggests that HIV, gibbsite, and amorphous Al are the most important P sorbing minerals in these samples in regard to P adsorption and P retention after four sequential desorptions. Surprisingly, total Fe oxides and amorphous Fe were not significantly related to P sorption for either the separated clay fractions or whole soils. This was unexpected since Fe minerals have been shown to adsorb large amounts of P (Hingston et al., 1974; Dao et al., 2001).

In addition to simple correlation, we also conducted multiple linear regressions (MLR) on each data set using the "STEPWISE" procedure in SAS software to determine the best fitting model. Results from the MLR in Table 3 agree with the results of the simple single correlations in that gibbsite, HIV, and amorphous Al were the best parameters used in predicting P retained from both adsorption and desorption. Kaolinite content was identified as the only significant variable in explaining P retention after four sequential desorptions from whole soils (negative relationship). The SAS software also identified total Fe oxides as an important model component in explaining P adsorption by the separated clay fractions. However, this was unexpectedly a negative relationship (Table 3).

To confirm these results, we repeated the adsorption and desorption experiment on pure clay minerals (goethite, hematite, gibbsite, poorly crystalline kaolinite, and well crystalline kaolinite). These minerals had a pH range of 5.5 to 6.0 and a WSP content <0.30 mg P kg^{-1}. Data presented in Fig. 4 shows that the two Fe oxides (goethite and hematite) adsorbed the highest amounts of P from the single point addition and retained a greater percentage of P after four sequential desorptions from the same samples when compared with gibbsite and kaolinite. This was expected since Fe oxides have a higher surface area (14–177 m^2 g^{-1}) compared with gibbsite (0.4–7.5 m^2 g^{-1}) and kaolinite (5–30 m^2 g^{-1}). The high P retention (both adsorption and desorption) by the Fe oxides is in contrast to the lack of a significant, positive relationship between P sorption and total Fe oxides or amorphous Fe among the soils used in this

Table 3. Results of the "STEPWISE" multiple linear regression analysis conducted by SAS on the relationship between mineral quantities and percentage of P retained from a single point isotherm ("adsorption") and four sequential desorptions ("desorption") performed on both whole soils and clay fractions. Analysis based on p value of 0.05.

Significant model parameters	Partial slope	Partial R-square	Model R-square	$C(p)$
	Clay fraction P retention: Adsorption			
Al_{ox}	0.004	0.65	0.65	98.8
Fe oxides	−5.592	0.17	0.83	48.6
gibbsite	5.078	0.11	0.94	16.6
	Clay fraction P retention: Desorption			
HIV	8.187	0.66	0.66	8.1
	Whole soil P retention: Adsorption			
HIV	19.555	0.86	0.86	1.9
	Whole soil P retention: Desorption			
kaolinite	−8.012	0.58	0.58	8.5

Reproduced from Soil Science Society of America Journal. Published by Soil Science Society of America. All copyrights reserved.

experiment. The results in Fig. 4 also confirm that kaolinite was not able to adsorb as much P relative to other P sorbing minerals and also was not able to retain as much of the adsorbed P after undergoing four sequential desorptions.

Previous studies have generally shown that Fe and Al oxides such as goethite, gibbsite, and amorphous materials possess a higher P adsorption capacity compared with 1:1 and 2:1 clay minerals. Jackman et al. (1997) conducted a P sorption study on 10 mineralogically diverse Hawaiian soils and found that the highest degree of P sorption was exhibited by Andisols that predominantly contained amorphous Fe and Al hydrous oxides, very fine-grained goethite, and no kaolinite. Medium sorption soils included the Oxisols that contained mostly illite, some goethite and gibbsite. The low P sorbing soils were Mollisols mostly rich in kaolinite containing very low amounts of Fe and Al hydrous oxides. Juo and Fox (1977) suggested that soils with very high P sorption capacities usually contain desilicated amorphous material, those with medium P sorption capacities contain 1:1 clay-size minerals and oxides, and those soils with low P sorption capacities contain 2:1 and 1:1 clay-size minerals with quartz. One similarity between these and other past studies is the conclusion that 1:1 clay minerals such as kaolinite tend to adsorb more P compared with 2:1 minerals. Our results somewhat contradict that notion since HIV (2:1) was better related to P retention (both adsorption and desorption) compared with kaolinite (Tables 2 and 3). In relation, Wijesundara (1996) found that the P adsorption maximum for both fertilized and nonfertilized Davidson soils were greater than for Tatum soils. In that study the two soils had nearly the same percentage of kaolinite (Davidson = 60% and Tatum = 62%) while the Davidson contained 27% HIV and the Tatum had none.

One possibility for this discrepancy (a 2:1 mineral adsorbing more P than a 1:1) may be that previous studies on P sorption in relation to soil mineralogy usually did not include soils that contained HIV, as HIV occurs predominantly in the southeastern USA (Rich, 1968). Hydroxy-interlayered-vermiculite is a unique 2:1 mineral in that its interlayer is intermediate to that of vermiculite (K, Mg, or Ca) and chlorite (Al or Mg hydroxy sheet). Although most 2:1 minerals possess little capacity to adsorb P because of few exposed terminal hydroxyls, HIV may be an exception to this rule of thumb due to its unique structure. The interlayer of HIV contains both K, Ca, or Mg (which holds the layers together) and disconnected sheets of amorphous Al hydroxides. Together they form "wedge zones" in the minerals that result in a highly exposed Al hydroxide with an increased surface area. The exposed Al hydroxide can potentially adsorb and retain P. As observed in this study, there was a significant and positive correlation between amorphous Al and HIV in the separated clay fraction ($r = 0.77$). Therefore this data set is unable to document that there is truly something unique about the structure of HIV that would make it a greater P sink compared with amorphous Al hydroxides in the soil (such as P being trapped in the interlayer), or if P adsorption by HIV is simply due to the Al hydroxide comprising the mineral (i.e., the ammonium oxalate extraction could simply be removing amorphous Al from the edges of the HIV). In addition, Saha and Inoue (1997) found that added P migrated into the interlayer of a synthetic HIV. The authors used x-ray diffraction on samples that had been saturated with 17 different concentrations of P (0–100 m*M* P) to show changes in the interlayer spacing with P adsorption. The authors also noted that P adsorbed onto synthetic hydroxy-interlayered smectites was poorly retained compared with the synthetic HIV.

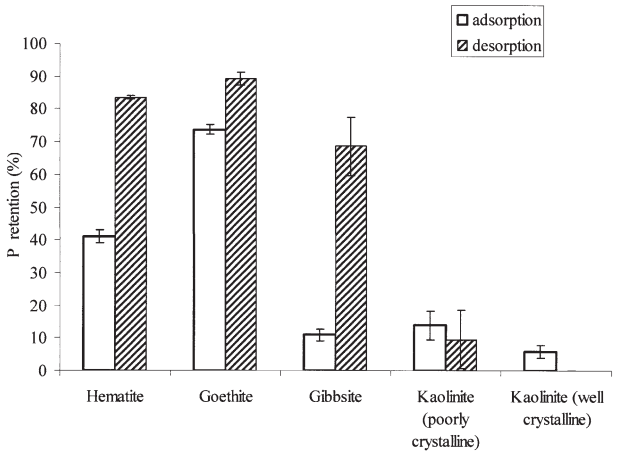

Fig. 4. Phosphorus retention by the pure minerals expressed as the percentage of added P that was absorbed during a single point isotherm (adsorption). Desorption expressed as P retained on samples after four sequential desorptions with 0.01 *M* $CaCl_2$ ([P remaining on sample after four desorptions/P remaining on sample after previous single point adsorption] × 100). Error bars indicate standard deviation. Least significant difference at $P < 0.05$ was 6.5 and 10.7 for adsorption and desorption, respectively.

Phosphorus Adsorption and Iron

As previously discussed, it was unexpected that there were no significant and positive correlations between P retention and total Fe oxides or amorphous Fe among whole soils and separated clay fractions (Tables 2 and 3). Again, this is in contrast to the literature and observations of the P adsorption and desorption isotherms conducted on pure minerals (Fig. 4). This suggests several possibilities: (i) P has a preference for adsorption sites in regard to Al and Fe, (ii) the different minerals are interacting with each other, and (iii) some co-correlations exist between Fe and other minerals.

Some observations in previous studies support the absence of a significant and positive correlation between P retention and Fe minerals (Tables 2 and 3) in that added P may have been preferred onto Al over Fe. This preference for Al may have resulted because the soil Fe was more saturated in P relative to Al. In a recent study, Khare et al. (2004) used x-ray absorption near edge spectroscopy (XANES) to identify P adsorbed onto mixtures of ferrihydrite (amorphous Fe mineral) and boehmite (amorphous Al mineral). The authors found that on clean samples, P was initially preferred for adsorption to Fe, but with increasing P addition

Reproduced from Soil Science Society of America Journal. Published by Soil Science Society of America. All copyrights reserved.

the Al mineral had an equal or greater affinity for P compared to Fe. Cabrera et al. (1977) concluded in a study of P adsorption onto various Al (gibbsite, boehmite, and corundum) and Fe (goethite, lipidocrocite, and hematite) oxides, that "Al oxides are more reactive than Fe oxides of similar specific surface areas."

Mineralogy and Runoff Dissolved Reactive Phosphorus

The retention of P during the sequential desorption experiments may be a good indicator of the potential for dissolved P release from soils not having received recent P amendments. Based on these results (Tables 2 and 3), soils not having received a recent P amendment (P is in a steady-state condition with the soil) and contain a low proportion of HIV to kaolinite (<0.5) would readily release DRP into runoff more easily compared with soils with a high proportion of HIV to kaolinite (>0.5). We were able to test this hypothesis by grouping soil types into "high" or "low" HIV/kaolinite and plotting their WSP values with runoff DRP concentrations from the simulated rainfall study. Data presented in Fig. 5a shows that for a given soil WSP value, soils with low HIV/kaolinite yield more DRP in runoff compared with soils with high HIV/kaolinite. Also, in an attempt to normalize the soils based on clay content we repeated the same procedure and expressed soil WSP as soil WSP/clay (Fig. 5b). This normalized data (Fig. 5b) indicates the same trend as previously described in Fig. 5a, at any given value of WSP/clay the low HIV/kaolinite soils resulted in more runoff DRP compared with high HIV/kaolinite soils.

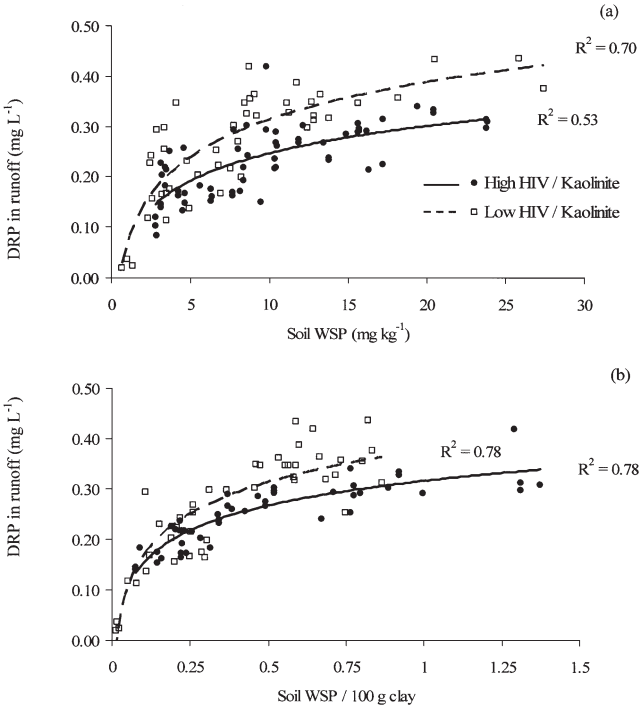

Fig. 5. Relationship between (a) soil WSP, (b) soil WSP/100 g clay and runoff DRP for soils considered "high" (>0.5) and "low" (<0.5) in the ratio of HIV to kaolinite based on soil mineralogical analysis of the nine different soil types. For each figure, correlation lines of "high" and "low" HIV to kaolinite were significantly different from each other at $P = 0.05$.

However, caution should be exercised in application of these results, as this rainfall study was conducted on soils that did not receive P amendments for over 1 yr. The observation that high HIV/kaolinite soils were able to retain P more tightly during a simulated rainfall may not hold true for soils receiving recent P amendments. Therefore, the best application of this data would be for soils that are no longer receiving P amendments in which the P is at steady state with the soil. For example, in Virginia permitted poultry operations with soils possessing M1-P values > 55 mg kg^{-1} can only receive a maximum single P application equivalent to the 3-yr crop removal rate. Thus, the low HIV/kaolinite soils among these would be expected to release more P in runoff compared to high HIV/kaolinite soils at similar soil P concentrations.

One problem in application of this research to field situations is that mineralogical analysis of soils may not be practical and the existing database of soil mineralogy (i.e., the soil survey) is based on subsoil mineralogy rather than the topsoil where runoff interacts with soil P. Therefore, it might be worthwhile to conduct mineralogical analysis on an extensive collection of representative topsoils to assess the amount of various clay minerals such as HIV and kaolinite in the topsoil of important agricultural soils. Studies on the effects of other clay mineral types (i.e., monmorillinite, chlorite, vermiculite) on DRP losses in runoff might also be necessary. Potentially, this would be easier and less expensive compared with conducting simulated rainfall on many different soil types having a range in soil test P to construct soil P vs. runoff DRP relationships for each soil type. The information could then be applied directly to a P index that utilizes the relationship between soil test P and WSP in assessing DRP losses in runoff from soil P pools.

CONCLUSIONS

Losses of P from soils not having recently received P amendments can still be significant in regard to critical P levels listed for flowing and lake waters (Vadas et al., 2004). Although soil P concentrations as determined by various extractions have proven to be well related to dissolved P losses in surface runoff, use of these relationships in predicting dissolved P losses is complicated due to differences among soil types. This study attempted to show that these different relationships may be due in part to differences in soil mineralogy, as ligand exchange of phosphate molecules in solution is mainly a function of mineralogy.

For the soils used in this study, clay content was not an important factor in regard to P sorption behavior, rather, soil mineralogy better explained variation in P adsorption and desorption. Phosphorus retained from P additions and sequential desorption experiments using separated clay fractions and whole soil samples was mainly correlated with HIV, amorphous Al, gibbsite, and

Reproduced from Soil Science Society of America Journal. Published by Soil Science Society of America. All copyrights reserved.

kaolinite. However, the correlation of kaolinite with P sorption was a negative relationship, indicating that kaolinite was not able to retain P throughout the sequential desorptions as strongly in comparison with the other minerals. This observation was confirmed by adsorption and desorption studies conducted on pure clay minerals. The significant and positive correlations of HIV with P retention was somewhat unexpected since 2:1 minerals are considered to have the least potential to adsorb P. This trend could be a result of P adsorbing onto Al hydroxides in the interlayer of HIV since amorphous Al was well related to HIV. Future studies using selective dissolution techniques could possibly answer this question.

Also unexpected was the result that Fe oxides and amorphous Fe were not significantly related to P retention. This could be due to co-correlations between Fe and other minerals, interaction between different minerals, or a preference of P adsorption onto certain Al minerals. Previous literature suggests that initially P may be preferentially adsorbed on Fe, but with further P additions Al may be preferred as an adsorption site.

Soils considered high in the proportion of HIV/kaolinite yielded less DRP in runoff for a given WSP and WSP/clay level when compared with the low HIV/kaolinite soil types. However, there are limits in the application of these results since the soils used in the rainfall study had not received P amendments for at least 1 yr before collection. This approach in using soil mineralogy to broadly group soils into categories for potential DRP losses could be easier and less expensive compared to determining the relationship between soil test P and runoff DRP for many different soil types using rainfall simulation studies.

REFERENCES

Bennoah, E., and D.K. Acquaye. 1989. Phosphate sorption characters of selected major Ghanaian soils. Soil Sci. 148:114–123.

Cabrera, F., L. Madrid, and P. De Arambarri. 1977. Adsorption of phosphate by various oxides: Theoretical treatment of the adsorption envelope. J. Soil Sci. 28:306–313.

Coale, F.J., J.T. Sims, and A.B. Leytem. 2002. Accelerated deployment of an agricultural nutrient management tool: The Maryland phosphorus site index. J. Environ. Qual. 31:1471–1476.

Dao, T.H., L.J. Sikora, A. Hamasaki, and R.L. Chaney. 2001. Manure phosphorus extractability as affected by aluminum- and iron byproducts and aerobic composting. J. Environ. Qual. 30:1693–1698.

Daverede, I.C., A.N. Kravchenko, R.G. Hoeft, E.D. Nafziger, D.G. Bullock, J.J. Warren, and L.C. Gonzini. 2003. Phosphorus runoff: Effect of tillage and soil phosphorus. J. Environ. Qual. 32:1436–1444.

Day, P.R. 1965. Particle fractionation and particle size analysis. p. 545–567. *In* C.A. Black et al (ed.) Methods of soil analysis. Part 1. Agron. Monogr. 9. ASA, Madison, WI.

Fox, R.L., and E.J. Kamprath. 1970. Phosphate sorption isotherms for evaluating the phosphate requirements of soils. Proc. Soil Sci. Soc. Am. J. 34:902–906.

Gburek, W.J., A.N. Sharpley, L. Heathwaite, and G.J. Folmar. 2000. Phosphorus management at the watershed scale: A modification of the phosphorus index. J. Environ. Qual. 29:130–144.

Hingston, F.J., A.M. Posner, and J.P. Quirk. 1974. Desorption of anions from hydrous oxide surfaces. J. Soil Sci. 25:17–26.

Jackman, J.M., R.C. Jones, R.S. Yost, and C.J. Babcock. 1997. Rietvield estimates of mineral percentages to predict phosphate sorption by selected Hawaiian soils. Soil Sci. Soc. Am. J. 61:618–625.

Jones, R.C. 1981. X-Ray diffraction line profile analysis vs. phosphorus sorption by 11 Puerto Rican Soils. Soil Sci. Soc. Am. J. 45:818–825.

Juo, A.S.R., and R.L. Fox. 1977. Phosphate sorption characteristics of some bench-mark soils of West Africa. Soil Sci. 124:370–376.

Khare, N., D. Hesterberg, S. Beauchemin, and S.L. Wang. 2004. XANES Determination of adsorbed phosphate distribution between ferrihydrite and boehmite in mixtures. Soil Sci. Soc. Am. J. 68:460–469.

Kunze, G.W. 1965. Pretreatment for mineralogical analysis. p. 568–577. *In* C.A. Black et al (ed.) Methods of soil analysis. Part 1. Agron. Monogr. 9. ASA, Madison, WI.

Kuo, S. 1996. Phosphorus. p. 869–920. *In* D.L. Sparks (ed.) Methods of soil analysis. Part 3 SSSA Book Ser. 5. SSSA, Madison, WI.

Loganathan, N.O., N.O. Isirimah, and D.A. Nwachuku. 1987. Phosphorus sorption by ultisols and inceptisols of the Niger Delta in southern Nigeria. Soil Sci. 144:330–338.

McKeague, J., and J.H. Day. 1966. Dithionite and oxalate-extractable Fe and Al as aids in differentiating various classes of soils. Can. J. Soil Sci. 46:13–22.

Moore, P.A., Jr., T.C. Daniel, and D.R. Edwards. 2000. Reducing phosphorus runoff and inhibiting ammonia loss from poultry manure with aluminum sulfate. J. Environ. Qual. 29:37–49.

Mortland, M.M., and W.K. Kemper. 1965. Specific surface area. p. 532–544. *In* C.A. Black et al (ed.) Methods of soil analysis. Part 1. Agron. Monogr. 9. ASA, Madison, WI.

Mozaffari, M., and J.T. Sims. 1994. Phosphorus availability and sorption in an Atlantic coastal plain watershed dominated by animal based agriculture. Soil Sci. 157:97–107.

Murphy, J., and J.R. Riley. 1962. A modified single solution method for the determination of phosphate in natural waters. Anal. Chim. Acta 27:31–36.

Parfitt, R.L. 1989. Phosphate reactions with natural allophane, ferrihydrite and goethite. J. Soil Sci. 40:359–369.

Pote, D.H., T.C. Daniel, A.N. Sharpley, P.A. Moore, D.R. Edwards, and D.J. Nichols. 1996. Relating extractable soil phosphorus losses in runoff. Soil Sci. Soc. Am. J. 60:855–859.

Pote, D.H., T.C. Daniel, D.J. Nichols, A.N. Sharpley, P.A. Moore, Jr., D.M. Miller, and D.R. Edwards. 1999. Relationship between phosphorus levels in three ultisols and phosphorus concentrations in runoff. J. Environ. Qual. 28:170–175.

Quinton, J.N., J.A. Catt, and T.M. Hess. 2001. The selective removal of phosphorus from soil: Is event size important. J. Environ. Qual. 30:538–545.

Rich, C.I. 1968. Hydroxy interlayers in expansible layer silicates. Clays Clay Miner. 16:119–123.

Saha, U.K. and K. Inoue. Phosphate adsorption behavior of hydroxyaluminum and hydroxyaluminosilicate-vermiculite complexes. 1997. Clay Sci. 10:113–132.

SAS Institute. 1999. SAS online. Ver. 8. SAS Inst., Cary, NC.

Schroeder, P.D., D.E. Radcliffe, M.L. Cabrera, and C.D. Belew. 2004. Relationship between soil test phosphorus and phosphorus in runoff: Effects of soil series variability. J. Environ. Qual. 33:1452–1463.

Southern extension research Activity (SERA)-17. June, 2004. National research project for simulated rainfall-surface runoff studies. Available online at http://www.soil.ncsu.edu/sera17/publications/National_P/National_P_protocol%20.pdf. (verified 6 May 2005). North Carolina State Univ., Raleigh.

Sims, J.T. 1998. Phosphorus soil testing: Innovations for water quality protection. Commun. Soil Sci. Plant Anal. 29:1471–1489.

Sims, J.T., R.O. Maguire, A.B. Leytem, K.L. Gartley, and M.C. Pautler. 2002. Evaluation of Mehlich 3 as an agri-environmental soil phosphorus test for the Mid-Atlantic United States of America. Soil. Sci. Soc. Am. J. 66:2016–2032.

Sharpley, A.N. 1995. Dependence of runoff phosphorus on extractable soil phosphorus. J. Environ. Qual. 24:920–926.

Sharpley, A.N., T.C. Daniel, J.T. Sims, and D.H. Pote. 1996. Determining environmentally sound soil phosphorus levels. J. Soil Water Conserv. 51:160–166.

Sharpley, A.N., B. Foy, and P. Withers. 2000. Practical and innovative measures for the control of agricultural phosphorus losses to water: An overview. J. Environ. Qual. 29:1–9.

Solis, P., and J. Torrent. 1989. Phosphate fractions in calcareous Vertisols and Inceptisols of Spain. Soil Sci. Soc. Am. J. 53:462–466.

Sposito, G. 1984. The surface chemistry of soils. Oxford Univ. Press, New York.

Torbert, H.A., T.C. Daniel, J.L. Lemunyon, and R.M. Jones. 2002. Relationship of soil test phosphorus and sampling depth to runoff phosphorus in calcareous and noncalcareous soils. J. Environ. Qual. 31:1380–1387.

Vadas, P.A., J.T. Sims, A.B. Leytem, and C.J. Penn. 2002. Modifying FHANTM 2.0 to estimate phosphorus concentrations in runoff from mid-Atlantic Coastal Plain soils. Soil Sci. Soc. Am. J. 66: 1974–1980.

Vadas, P.A., P.J. Kleinman, and A.N. Sharpley. 2004. A simple method to predict dissolved phosphorus in runoff from surface-applied manures. J. Environ. Qual. 33:749–756.

Van Olphen, H., and J.J. Fripiat. 1979. Data handbook for clay materials and other non-metallic minerals. 1st ed. Pergamon Press, Elmsford, NY.

Virginia Department of Conservation and Recreation (DCR). 1995. Virginia nutrient management standards and criteria. Virginia DCR, Richmond, VA.

Wijesundara, S.M. 1996 Relationships of soil test phosphorus with soil properties and phosphorus forms. Ph.D. Diss., Dep. of Crop and Soil Environmental Sciences, Virginia Polytechnic Institute and State University, Blacksburg, VA.

Reproduced from Soil Science Society of America Journal. Published by Soil Science Society of America. All copyrights reserved.